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14. ABSTRACT

Under support from this DURIP grant, a unique high resolution kHz repetition rate Ti: Sapphire laser has been purchased. Considerable custom modifications were done to produce a stable, broadly tunable light source that cover the near IR through deep UV. A Nd: YAG laser was also rebuilt as a cavity dumped, injection seeded, Q-switched laser. The two lasers are being used for stimulated Raman Scattering experiments on pH_2 clusters in the framework of a program meant to investigate the properties of light-atom seeded solid hydrogen in relation to its possible use as improved rocket fuel.

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BROADLY TUNABLE, HIGH AVERAGE POWER, NARROW BANDWIDTH LASER SYSTEM FOR CHARACTERIZATION OF HIGH ENERGY DENSITY MATERIALS

K. K. Lehmann and G. Scoles
Chemistry Department
Princeton University
Princeton, New Jersey 08544

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Final Report

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1. Introduction

Investigations into the formation, storage, and reactions of novel High Energy Density Materials (HEDM) are an important research frontier for the Department of Defense.[1] Modest improvements in the specific impulse over presently available fuels will dramatically improve the performance of rocket-based propulsion systems. Advances in this area promise not only to address weapons-related needs of the Armed Forces, but to improve the flexibility and capabilities of the electronic "eyes and ears" of the United States. Tremendous commercial applications also exist for improved rocket fuels in providing the infrastructure for wireless global information systems.

The research program established by us at Princeton, with the continued support of the U.S. Air Force, aims at the improvement of the propellant qualities of solid hydrogen rocket fuel through the introduction of atomic dopants.[2] To create a HEDM, the hydrogen and atom mixture must be metastable, i.e., trapped in a chemically high energy state.

Our work has focused on the properties of metal atoms and their small oligomers in cryogenic solids and liquids, in order to create the knowledge base from which the chemical dynamics of such systems can be characterized and, ultimately, predicted. Our current research focus is on the formation and characterization of small metal clusters with novel properties, on the study of metal-hydrogen cluster interactions and on the investigation of the possible superfluid behavior of parahydrogen clusters.

Our earlier AFOSR-funded program helped establish the new field of doped quantum cluster spectroscopy as one of the most efficient ways to access and study very cold molecules and chemical metastability. The February 2001 issue of Physics Today contains a review[3] of the work on liquid helium nanodroplet spectroscopy, which makes clear the potential of this technique for both the synthesis and investigation of metastable systems that cannot be prepared in any other way. The Journal of Chemical Physics has recently (December 8, 2001) published a special issue dedicated to this new area. As another spin-off of our earlier AFOSR-funded work we have developed a second machine, with support from the National Science Foundation, that is investigating the formation, stabilization, and chemical dynamics of high-spin states of small radicals in liquid helium. The focus of the NSF-funded program is on the chemical dynamics of open-shell species at very low temperatures. It is clear that there is great potential synergy between these two programs, and that knowledge acquired under the NSF-supported program will contribute towards establishing the range of conditions under which HEDM species can be synthesized in this unique environment. Both research programs use spectroscopy to determine properties of novel chemical species and their dynamics following photoexcitation. As our detection techniques are mostly based on energy deposition or laser-induced emission (as opposed to laser beam attenuation), access to powerful and widely tunable laser sources is essential to our progress.

In this report we describe work carried out with support of the DURIP program, which has resulted in a new and unique laser facility that is capable of high repetition

rates (1-5 kHz), high power levels, a broad tunability range, and an unprecedentedly narrow bandwidth for such a pulsed source. Previous work in our HEDM program was limited mainly by the wavelengths we could achieve using continuous wave dye and Ti:Sapphire lasers. We also had limited access to an optical parametric generator/amplifier with 1 kHz repetition rate. This system was available to us as one user among many, and required the laser beam to be transported from another floor to our laboratory. Furthermore, that laser system has much poorer spectral resolution than what is needed for many experiments.

Rydberg-type electronic excitations, as are commonly observed in metals and metallic clusters, are often quite spectrally broad when these are dissolved in hydrogen or helium nanoclusters or in a bulk condensed phase[(4,5)], which limits the information that can be extracted. Though some electronic transitions, due to valence or inner core transitions, have been shown to be spectrally narrow, almost all ro-vibrational transitions of polyatomic molecules studied to date in liquid helium or p-H_2 matrices have narrow transitions. A particularly attractive, but technically more difficult way to spectroscopically probe doped hydrogen clusters would be to probe the ro-vibrational transitions of the host hydrogen medium. These transitions are expected to be sensitive to the presence and nature of the dopant species and to be much narrower (and, therefore, richer in information) than the electronic transitions of the seeded metals. There are two ways of probing such transitions: by Stimulated Raman Scattering (SRS), which should be applicable to all hydrogen clusters, even undoped ones, or via the impurity-induced ro-vibrational transitions, as they have been observed in doped bulk p-H_2 crystals by Fajardo et al.

We will describe here the progress that we have made in constructing a laser system that will allow such experiments to be performed. We have performed SRS measurements in a static gas phase sample and stabilized the Ti:Sapphire laser to the level necessary for the SRS measurements in a beam of p-H_2 clusters. It is anticipated that these beam measurements should be forthcoming soon. Furthermore, the frequency-doubled Ti:Sapphire laser output has been used to study the dynamics of NO_2-doped helium clusters following excitation of the NO_2 to levels above the gas phase dissociation threshold.

2. The stimulated Raman pumping scheme

In order to pump the ro-vibrational transitions of hydrogen clusters doped with light metal atoms or their oligomers, thus constituting a candidate HEDM material, we have devised a stimulated Raman pumping technique which is quite similar, in principle, to that which we have successfully employed in detecting infrared transitions of molecules seeded in liquid helium or solid hydrogen clusters.[6] According to this scheme, electromagnetic energy is resonantly deposited in a beam of seeded clusters via excitation of the guest molecules. The relaxation of this excitation into the clusters (which are maintained at their low temperatures by evaporative cooling) results in evaporation, which in turn leads to a decrease in the energy flux of the beam. Alternatively, if the excitation does not relax, its energy remains in the beam and produces a signal of the opposite sign. For the detection of these changes in beam energy, we are using the well-tested technology of bolometric detection. In the present case, we use a specially doped Si bolometer that senses the temperature of a sapphire "beam receiver" kept at the relatively high temperature of ~5 K in order to avoid condensation of the H_2 beam on the receiver surface, which would decrease the detector sensitivity and make its response time much longer.[7] Based upon the observed noise in the instrument and the known responsivity of the detector, can observe a change in the beam energy of 0.5 pW per $\sqrt{\text{Hz}}$ bandwidth, which corresponds to the vibrational excitation of 6×10^6 H_2 molecules per second, or a fraction of one part in 3×10^5 of the observed ground state hydrogen beam flux on the bolometer. Evaporation will lead to a slightly larger absolute signal, since the evaporation energy, 92 K per H_2, is somewhat less than the kinetic energy per H_2 molecule, ~125, that is lost from the beam upon evaporation. This calculation assumes a nozzle temperature of 50 K, which in previous work from our laboratory was a typical operating temperature.

The stimulated Raman pumping scheme is shown in Figure 1. The pump wave will be the 738 nm output of a Ti:Sapphire laser, and the Stokes wave will be the 1064 nm output from a Nd:YAG laser. We assume each laser has an energy of 1 mJ, has a

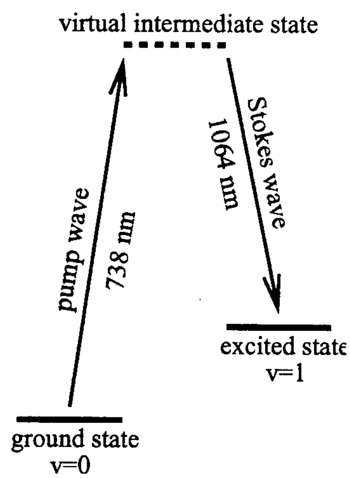

Figure 1. Excitation scheme for Stimulated Raman Scattering in H_2 molecules. The H_2 molecules are stimulated to inelastically scatter a "pump" photons, creating "Stokes" photons and vibrationally excited molecules.

pulse width of 10 ns full width at half maximum (FWHM), is focused down to about 1 mm^2 cross sectional area (to approximately match the size of the bolometer) and thus has a peak intensity of 10 MW/cm^2, and that the Raman transition has a width of ~100 MHz. Using these parameters, we calculate, based upon the Raman cross section of H_2 (~5×10^{-30} cm^2), that about 0.3% of the hydrogen molecules in the focal volume of the lasers will be pumped to the first vibrationally excited state. We have purchased gold-coated metal mirrors that can be used to construct a multipass cell (~50 passes); this should allow about 5% of the molecular beam to be illuminated by the lasers. This leads to an estimated signal-to-noise ratio of 40:1 for one second of integration.

It should also be possible to generate 2.4 μm radiation by difference frequency mixing of the 738 and 1064 nm radiations in a nonlinear crystal such as periodically poled $LiNbO_3$, for which essentially unit quantum conversion is estimated. With this radiation, H_2 molecules near dopants can be pumped directly. Conservatively assuming an IR energy of 100 μJ/pulse, or an intensity of 1 MW/cm^2 when focused down to the 1 mm^2 spot size, and assuming a ~100 MHz FWHM for the vibrational transition, we can estimate that this pulse will saturate any transition with more than ~2×10^{-3} Debye transition moment (1 Debye = 3.3×10^{-30} Cm), which corresponds to an induced transition intensity more than one thousand times weaker than that of a typical C-H stretching fundamental (~0.08 D). Anderson et al. found that doping a p-H_2 matrix with HCl induced a H_2 absorption with an integrated strength ~2% of that of the HCl itself.[8] Saturation of such a dopant-induced dipole transition in the hydrogen should lead to a similar signal to noise ratio as for the SRS transition given above.

3. The laser system

3.1. The tunable Ti:Al_2O_3 laser

The heart of the new laser system is an Indigo Ti:Al_2O_3 system[9] manufactured by Positive Light of Los Gatos, CA., pumped with 10 W from an Evolution-X intracavity-doubled Nd:YLF laser. While the specifications for the laser promised high power (>1 mJ) and single mode performance (< 60 MHz linewidth), as delivered it did not meet the latter specification. We will now describe the modifications that have allowed us to obtain the original specs of a stable single mode output.

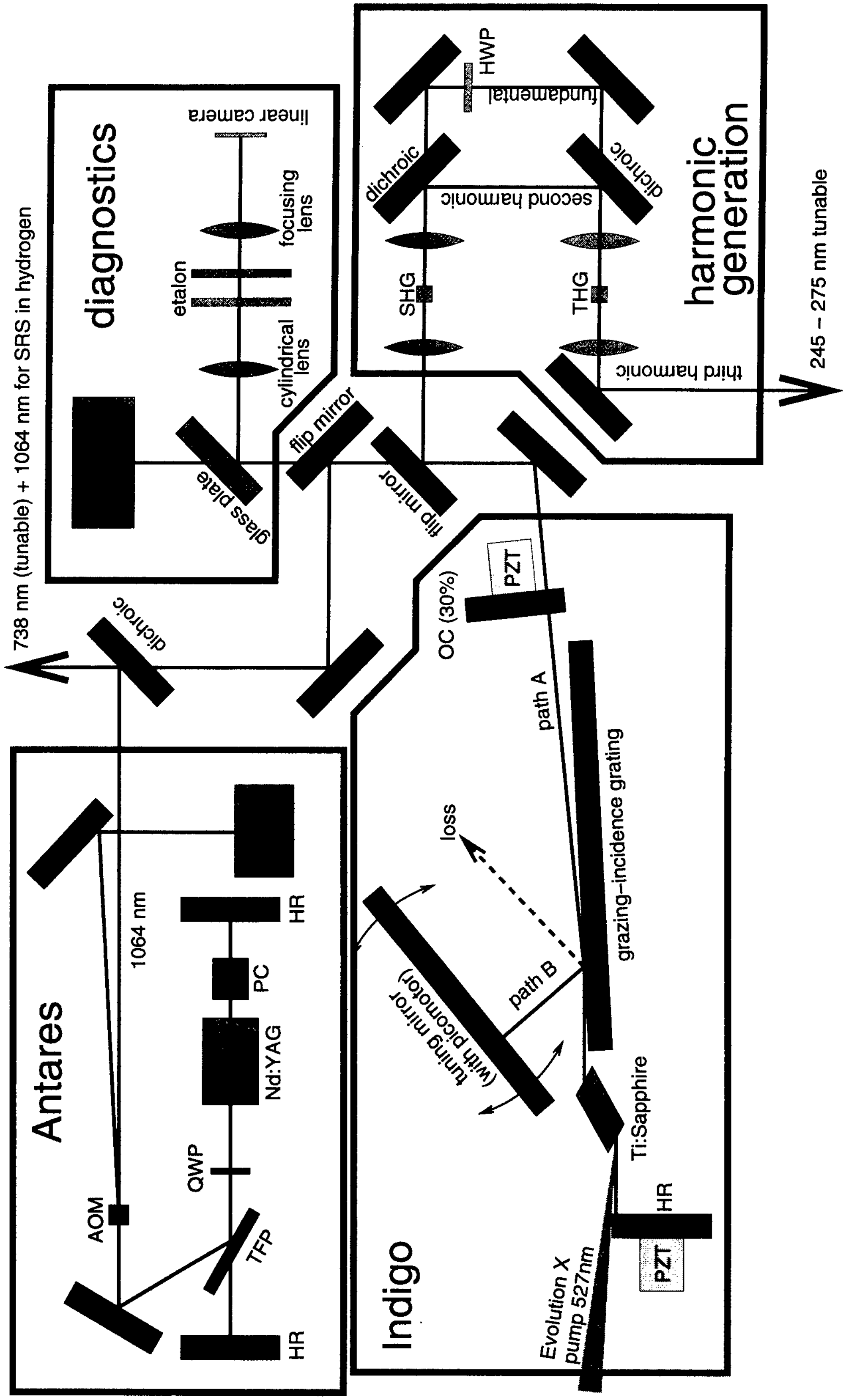

Figure 2. Setup of the laser system. The Indigo is a tunable, pulsed single-mode $Ti{:}Al_2O_3$ laser that can be frequency-doubled and -tripled. The Antares is a pulsed Nd:YAG laser synchronized with the Indigo, to be used for stimulated Raman scattering or frequency mixing with the Indigo. The diagnostics are used both for wavelength measurements and mode stabilization of the Indigo.

The single-mode output of the Indigo is realized by use of a modified Fox-Smith resonator[10] consisting of a high reflector (HR), an output coupler (OC), a nearly grazing incidence grating, and a tuning mirror (see Figure 2). This design features a compound cavity. The HR, grating, and tuning mirror form a "Littman" cavity (path A) which has a line width of a few tenths of cm^{-1} when running alone; because of the low gain and grating reflectivity, this cavity is kept below threshold. A fraction (~30%) of the zero-order reflection off of the grating is reflected back towards the gain medium by the output coupler (path B). Interference of the two light paths upon recombination at the grating leads to a wavelength dependence of the effective feedback amplitude of the coupled cavity. The resulting interference pattern has a free spectral range of $(2\Delta L)^{-1}$, where ΔL is the difference in length between paths A and B. This pathlength difference is selected so that only one "order" of this Fox-Smith interference pattern is within the pass-band provided by path B. Conditions of constructive interference both lower the threshold of the laser and allow for single-mode performance when the cavity mode, the interference maximum, and the grating pass-band all are well aligned. However, the laser, as delivered, did not have a sufficient number of actuators to control all three conditions, and had no mechanism for monitoring the laser output characteristics in order to allow rational control of the actuators. As the intracavity path lengths drifted, one obtained multimode output and substantial timing jitter between pump laser and Indigo output, since changes in effective feedback changed the laser build-up time.

The lasing threshold of the Indigo resonator is reduced if we have constructive interference between the two light paths. If all other cavity elements are fixed, we can change the length of path A by displacing the OC, which is done by applying a voltage to the OC PZT. This shifts the absolute wavelengths at which constructive interference occurs, and we can thus make sure that at the maximum of the wavelength selectivity of path B we simultaneously have constructive interference of the two light paths. Furthermore, we must place the HR at a position where both light paths simultaneously have a node, so that the two light paths actually form an eigenmode of the laser cavity. We do this by applying a voltage to the HR PZT. This is a modification to the original design of the Indigo by Positive Light, Inc., in which there was no provision for such fine-tuning. We have found, however, that stable single-mode operation of the Indigo cannot be achieved without this additional degree of freedom.

We have constructed a computer based feedback system that observes the spectral quality of each laser shot of the Indigo by use of a plane-parallel étalon (with Free Spectral Range (FSR) equal to 4.4 GHz) whose output is imaged with a linear camera. Careful adjustment is made to put the camera precisely in the focal plane of a lens that follows the étalon, which leads to known frequency dispersion of the laser output spectral density across the camera (up to the expected "aliasing" by the FSR of the étalon). This FSR is selected to allow a clean separation of growing power in either adjacent cavity modes (~800 MHz) or adjacent orders of constructive interference between the two beams returning to the grating (Fox-Smith modes, ~3 GHz). The control electronics reads the linear camera, test for optical power at the expected positions corresponding to the two possible mode hops, and then adjusts the voltages on the two cavity PZTs accordingly. Misplacement of the HR is detected by observing the emergence of neighboring cavity modes. Misplacement of the OC is detected by the emergence of

neighboring Fox-Smith modes. With this system in place, single-mode operation of the Indigo can usually be established within a few hundred milliseconds. As the tuning mirror is rotated slowly and thus the wavelength selected by path B is scanned, the positions of the HR and OC mirrors are adjusted continuously, allowing smooth tuning of the single-mode output of the Indigo. The linear tunability is now only limited by the gain medium and the cavity optics.

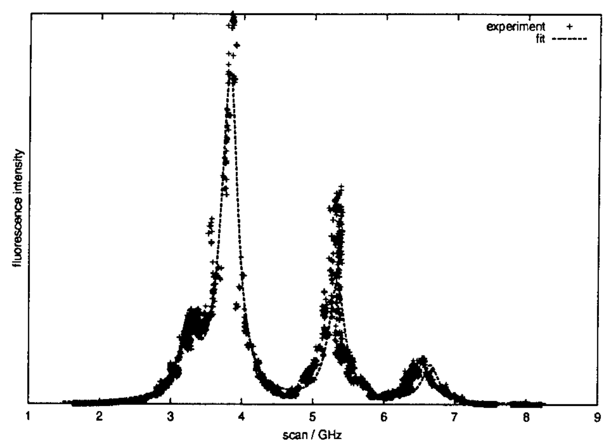

Figure 3. The two-photon fluorescence spectrum of gas-phase rubidium, as measured with the Indigo. The main peak corresponds to the $5S_{1/2}$ (F=3) $\rightarrow$ $5D_{5/2}$ (F=5) transition in ^{85}Rb, and is at 385 285 142 378.280 ± 2 kHz

With stabilization, the Indigo puts out single-mode radiation that is likely to be transform limited (~50 MHz) by the pulse duration of approximately 10 ns. Figure 3 shows a scan of the two-photon absorption spectrum of Rubidium vapor near 778.1 nm. The spacing of the features reflects the hyperfine splitting of the ground states of ^{85}Rb and ^{87}Rb. The full width half maximum of the features, 340 MHz FWHM, is less than the calculated Doppler broadened value of 520 MHz, likely due to some Dicke narrowing in the cell. We plan in the near future to make a Doppler-free measurement to quantify the time averaged spectral width of the locked Indigo laser. The timing jitter of the locked Indigo output, relative to the pump pulse, is no more than 2 ns, i.e., a small fraction of the pulse width. The latter feature is required for synchronization of the Indigo output to other lasers. Pumped by a 10 W Evolution X diode-pumped, intra-cavity frequency-doubled Nd:YLF laser, the Indigo can deliver up to 1.5 mJ pulses around 800 nm at 1 kHz repetition rate. Positive Light has promised to replace, at no cost, the Evolution X with the Evolution XXX, which should provide more than 25 W at 1 KHz and 30 W at 3 kHz. With the new pump laser, we expect an even better performance of the system, allowing essentially the same energies per pulse at thrice the pulse repetition frequency. The wavelength of the Indigo radiation is monitored with a Burleigh WA-4500 wavemeter, also purchased under this grant. The rubidium vapor experiment provided a correction for dispersion in the wavemeter, which uses a 633 nm laser as its absolute wavelength reference.

The specs of the Indigo called for broad band tunability (690-920 nm), but as supplied it was only able to tune near the peak of the Ti:Sapphire gain, 770-830 nm. One

problem is that one arm of the cavity has no wavelength selectivity and that feedback on this arm near the gain maximum of Ti:Sapphire will take over from the feedback selected by the grating. This occurs when the net round trip gain of the cavity near gain center from path A alone exceeds the net round trip gain off of the gain peak despite the extra feedback that the constructive interference of the Fox-Smith design provides. We have been able to extend the tuning range of the Indigo towards the blue by purchasing a second set of cavity mirrors, "short band optics", that are designed to maximize feedback on the high frequency side of the gain maximum, while suppressing feedback near the region of maximum gain. With this optics set, we have realized laser output from 720-780 nm. It is believed that with an additional set of "long wavelength" optics, the tuning range of the laser may be extended out to 920 nm, the original spec of the laser.

Indigo Harmonics Generation

The high peak power of the Indigo invites generation of second- and higher harmonic laser radiation. The specs provided by Positive Light included the capability to generate the second through the forth harmonics. The laser arrived with second harmonic capability, and we were later supplied with the third harmonic generation components. The second-harmonic generation (SHG) is done by focusing the fundamental into a critically phase matched (angle-tuned) LBO crystal, and produces up to 200 μJ pulses around 400 nm, which matches the original spec of the laser. Higher conversion efficiency is expected from use of BBO, but at the cost of reduced beam output quality, due to a greater walkoff angle of that material. Third-harmonic radiation is generated (THG) by co-focusing the fundamental and the second harmonic into an angle-tuned, Type I phase matched BBO crystal. Since the polarization of the second harmonic is orthogonal to the fundamental due to birefringence phase matching in the LBO crystal, we rotate the plane of polarization of the fundamental by 90° with a half-wave plate (HWP) after separating it from the second harmonic with a dichroic mirror. We can produce up to 3.5 μJ of UV light at 260 nm in pulses of about 7 ns length. While this represents a useful photon flux at this wavelength and bandwith, it is well below the original specifications, 75 μJ, and we plan to work with Positive Light to improve the third harmonic conversion efficiency. We expect to receive the components for fourth-harmonic generation (FHG) soon. This is based upon sum frequency mixing of the THG output with the residual fundamental, which allows for a greater phase matching range. The FHG capability will allow us to extend the range of accessible wavelengths into the vacuum UV; Positive Light specifies an output of at least 2 mW at 193 nm. We custom fitted all the harmonic-generation crystals with picomotor screws, which allow software control of the phase matching angle as the Indigo is scanned in frequency.

3.2. Nd:YAG Laser System

While the single mode Ti:Sapphire laser and its harmonics provide substantial spectral coverage, there are still large regions in the visible and UV that are not accessible with this laser source alone. Unlike the case of lower repetition rate, high pulse energy (>10 mJ) sources, we cannot effectively use Raman Shifting to "fill in" the spectrum. More importantly for our AFOSR project, we want to be able to generate vibrational

excitation in molecular hydrogen (and its isotopic variants). To this end, we have constructed a pulsed Nd:YAG laser system from an available Coherent Antares[11] laser that we had previously used to pump our picosecond dye lasers.

As discussed above, our design goal is to be able to do vibrational pumping of molecules, especially molecular hydrogen, by both Stimulated Raman Scattering and by dopant-induced IR absorption. IR radiation near 2.4 microns for such excitation can be generated by difference frequency mixing the output of the Indigo and a Nd:YAG fundamental output. Stimulated Raman scattering can be used to excite the k=0 vibrational exciton, which in a p-H_2 crystal is known from the work of Oka to have a spectral width of less than a few MHz wide. This SRS excitation can be generated by simultaneously exposing the p-H_2 clusters to these two radiation fields. What is needed for these applications is a Nd:YAG laser source that can be time synchronized to the Indigo laser to better than the width of the two laser pulses, have power at least comparable to that of the Indigo, and also has a line width near the Fourier Transform Limit. We decided that we needed an injection seeded, Q-switched cavity-dumped laser to meet these requirements.

A schematic of the Nd:YAG laser we built is shown in Figure 2. Gain is provided by a cw flashlamp pumped Nd:YAG module. The cavity starts in a low Q state, allowing build-up of gain in the Nd:YAG rod. Light from a Lightwave S-100 seed laser (~2 mW) enters the cavity from the intracavity thin film polarizer (TFP) and then makes one and a half round trips of the cavity (with orthogonal polarization) before being rejected by the same polarizer. The Q of the cavity is raised by shorting one electrode of an intracavity KD*P Electro-Optic Pockels cell[12] which converts it to a 1/4 wave plate. This "traps" light of one polarization inside the cavity. This wave builds up to a peak intracavity power of about 100 kW in about 2 μs. Near the peak of this intracavity pulse, the other side of the Pockels cell is shorted, returning the cavity to a low Q state, and dumping the intracavity stored laser energy in one round trip time, ~10 ns. The timing of this dumped pulse is derived, with time delay, from the green pump pulse of the Indigo. The relative timing jitter of the Indigo and Nd:YAG outputs is less than 2 ns. The Nd:YAG output then counter-propagates the path on which the seed light had entered the cavity. To separate these waves, and to protect the seeder from optical damage, the seed light enters the cavity as the first order diffraction from an acousto-optic modulator (AOM). The build up time of the Nd:YAG regenerative amplifier is sufficient that the AOM diffraction can be completely turned off before the cavity-dumped output pulse arrives, and thus this wave passes with little attenuation through the AOM. The output energy of the Nd:YAG laser is about 2 mJ/pulse when run at 1 kHz. The output is smooth and reasonably close to TEM_{00}.

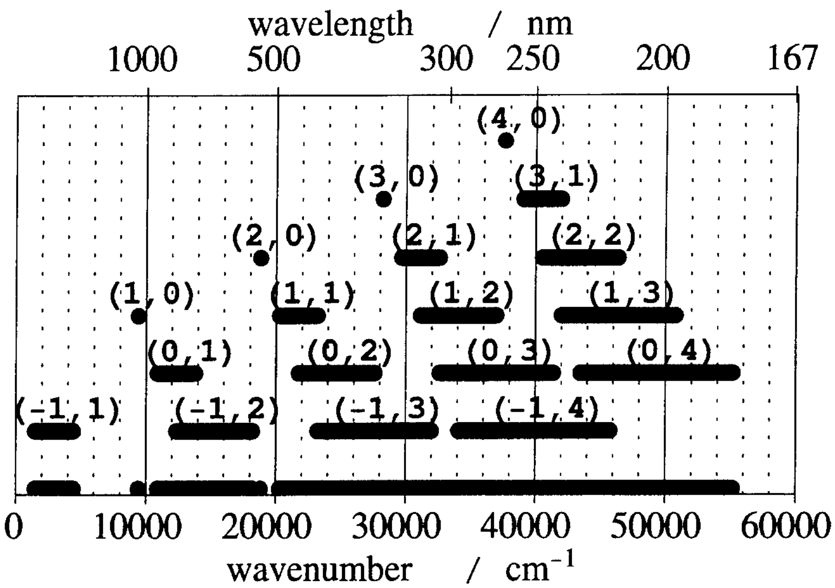

Figure 4. Spectral regions accessible with the Indigo $Ti:Al_2O_3$ in combination with the Antares Nd:YAG. The label (m,n) refers to mixing the mth harmonic of the Nd:YAG with the nth harmonic of the $Ti:Al_2O_3$. For example, (-1,3) is the difference frequency between the tripled $Ti:Al_2O_3$ and the fundamental of the Nd:YAG. The bottom line summarizes the accessible wavelength ranges. A fundamental tuning range of 720-920 nm was assumed for the Indigo.

The free running line width of the Nd:YAG laser has been measured at ~0.6 cm^{-1}, which is greater than our requirements. Seeding should ideally produce a single longitudinal mode output. However, that requires an active locking of one of the modes of the Nd:YAG cavity to the seeder frequency by adjusting the Antares cavity length. Attempts have been made to use the "build-up time" minimization circuit that came with the seeder (which was taken from an old Continuum 20 Hz Nd:YAG laser that is not longer run injection seeded) to do this locking, but so far without success. We do believe it should be possible to do the locking by monitoring, before firing the Q-switch, the polarization state of light leaking out of the end mirror on the Q-switch side of the cavity but this has not yet been tested. Even without such locking, the seeding should produce almost all the energy in the two modes on each side of the seed frequency, giving an effective line width of ~100 MHz. By placing the Q-switch close to one end mirror of the cavity, we have found, as predicted, that the buildup time reduction produced by seeding is stable, implying little modulation of intracavity seed intensity when the Q-switch is thrown. The wavelength output of the Nd:YAG laser has been monitored by frequency doubling a small part of its output and putting this into the Burleigh wavemeter.

In principle, we should be able to frequency double the Nd:YAG laser output in noncritically phase matched LBO with near unity conversion efficiency. Third and fourth harmonics can be generated in BBO. These outputs can be used directly for experiments, such as photodissociation, and can also be mixed with different harmonics of the Ti:Sapphire laser. IR radiation from 2.2-6.8 μm can be generated by frequency mixing the 720-920 nm output of the Indigo with the 1.064 μm Nd:YAG fundamental output. Use of periodically poled $Li:NbO_3$ should allow this mixing to be done with

nearly unit quantum efficiency, thus generating hundreds of μJ of IR radiation. Figure 4 shows the different spectral regions that can be reached in this way, given the expected tuning range of the Indigo laser.

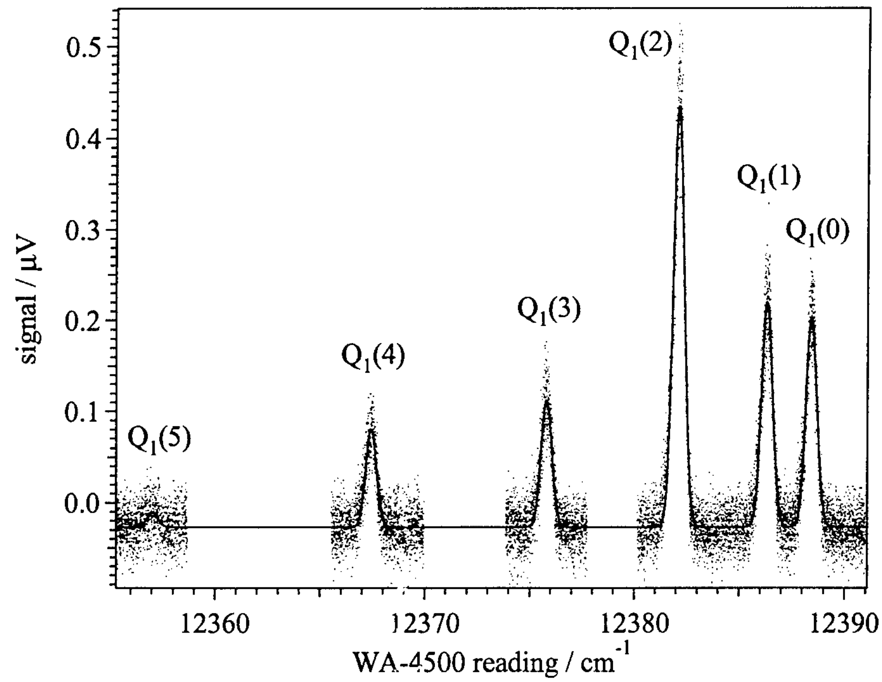

Figure 5. The vibrational Raman spectrum of D_2, taken in a photoacoustic cell at 450 Torr of D_2 and 150 Torr of CO_2. The solid line is a Gaussian fit with equal width for all peaks.

As an initial test of our ability to simultaneously use the Indigo and Antares lasers, we measured the Raman spectrum of D_2 in a cell, detected by the photo-acoustic method. Figure 5 shows the spectrum so obtained. This spectrum was taken before we had successfully implemented the injection seeding of the Nd:YAG laser and before we had obtained the "short wavelength" optics for the Indigo. The former explains the observed line width, and the latter the use of D_2 instead of H_2 for this test.

The frequency-doubled output from the Indigo laser has been used to study the spectrum of NO_2 in helium droplets when excited in the region of the gas phase dissociation threshold, 398 nm. Excitation of NO_2 in helium droplets generated no detectable fluorescence signal even below the threshold, likely due to rapid relaxation. However, absorption could be detected by bolometrically detected helium beam depletion. It was expected that when excited above dissociation threshold, the NO ($^2\Pi$) and O (^3P) states generated will recombine about two thirds of the time as spin-quartets rather than the spin-doublets that are strongly coupled to the ground state. If any of these quartets are metastable, like we earlier found for the high spin states of alkali dimers and trimers on helium droplets, then we would expect to find a drop in the depletion signal, since the energy used to break the NO-O bond would not be available for evaporation of helium from the droplets. Instead, we detected no drop in depletion signal even when the excitation energy was 2000 cm^{-1} above the gas phase dissociation threshold. This result

suggests either that NO+O recombination does not form any metastable quartet states of NO_2, or that the vibrational cooling of the hot NO_2 molecules by the helium is sufficiently fast that molecules are quenched below the dissociation energy before dissociation occurs. The dissociation of $NO_2 \sim 1$ ps in the gas phase at the highest energy probed.

4. Outlook and work in progress

The new laser system has opened an exciting new window on doped hydrogen clusters. As mentioned above, electronic spectra of dopants in hydrogen or helium often have diffuse spectra due to the large change in the size of the dopant as well as due to rapid quenching and/or photochemically induced reactions. In contrast, the vibrational Raman transitions of hydrogen should be extremely sharp, including those of hydrogen molecules located near a dopant.[13] Such spectroscopy on hydrogen nanoclusters nicely complements the recent HEDM activity of Mario Fajardo at Edwards AFB, giving us access to an increased number of high energy species which can be uniquely synthesized and characterized in the cluster environment.

The outputs of the Ti:Sapphire and Nd:YAG lasers can also be difference frequency mixed in periodically poled lithium niobate and other "engineered" nonlinear materials to generate high average power, very narrow line width radiation in the 2-6.5 micron spectral region.[14] Such radiation will also open up new avenues for our HEDM study, including structural studies of metal hydrides formed in hydrogen clusters, either by direct insertion or after photochemical excitation of the metal species.

The question of most fundamental interest to be asked about hydrogen clusters as spectroscopic hosts relates to their possible superfluid behavior. In recent years, the experimental feasibility of observing a superfluid phase of parahydrogen (p-H_2) has been investigated in various contexts;[15-19] to date, the existence of such a phase has not been conclusively proven. In particular, the effects of other species, used as a spectroscopic probes, may strongly perturb the hydrogen, as hydrogen-dopant interactions are typically considerably stronger than those of hydrogen with itself.

The goal of an ongoing effort here at Princeton is to produce ultracold p-H_2 droplets of a few hundred to a few thousand molecules in a supersonic expansion,[20] which will be spectroscopically investigated using stimulated Raman scattering (SRS). We plan to study both pure p-H_2 clusters and clusters grown inside of helium droplets, which will allow for cooling down to 0.38K. The p-H_2 droplets have good prospects for being superfluid because both their small size and their very short lifetime in the experiment strongly suppress the nucleation of freezing: it may, therefore, be possible for them to be supercooled so much below the triplet point of p-H_2 for Bose-Einstein condensation to occur. While direct spectroscopic tests of the superfluid state are perhaps subject to interpolation, theory clearly predicts that a liquid state of pure p-H_2 at 0.38K (a factor of ten below the ideal gas Bose-Einstein condensation temperature) must be a superfluid. The Raman spectrum has clear features, such as the splitting of the $J = 2$ state in the crystal field, which can distinguish the liquid from solid phase.

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